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Description of organic compound vapor-phase sorption by geosorbents: Adequacy of the isotherm approximation

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Abstract

The approximation of isotherms of vapor-phase sorption of organic compounds (OC) is a long-standing problem. It is especially difficult to solve in case of natural heterogeneous sorbents (soils, sediments, aquifers, etc.) since these sorbents contain sites with different sorption activity. The aim of this work was the statistical evaluation of the adequacy of the approximation of isotherms of vapor-phase sorption of OC by geosorbents in water-unsaturated conditions by employing various fitting equations. Vapor sorption isotherms were measured by the static headspace gas-chromatographic analysis method for 27 various organic sorbates (13 hydrocarbons and 5 chlorinated hydrocarbons, 7 oxygenated and 2 nitrogenated OC) on geosorbents (6 soils typical for Middle Russia regions, separate soil layers of 2 dark-gray forest soils, natural zeolite-containing material and bentonite clay, and two clay-humic complexes). The computer-assisted special sorption database with the corresponding software was created, and on the whole, 103 experimental sorption isotherms (86 isotherms measured and 17 taken from the literature) were used for the approximation. The adequacy of isotherm approximation by different sorption models was compared: Brunauer–Emmett–Teller (BET), modified BET (MBET), Pickett–Dellyes (PD), Guggenheim–Anderson–De Boer (GAB), Aranovich–Donohue (AD), Hinz (HZ) and polynomial (PN) equation. For the comparison of the adequacy of isotherm approximation by different equations, the following three criteria were used: (a) $s_{5\%}$—the average probability of the location of experimental sorption values within the range of 5% of the theoretical curve; (b) two interconnected parameters: R^2—the square of correlation coefficient and k—the slope tangent for the linear regression (V^E; V^T) at various sorbate activities; (c) $\overline{D}$—relative sample variance as a characteristics of the optimal ratio between numbers of parameters of the fitting equation and its approximation quality. For the description of the vapor sorption of OC by geosorbents, the new MGAB equation (the modified GAB equation) was suggested. It is characterized by the optimal ratio between the 'complexity' of an equation (MGAB is a four-parametrical equation) and its approximation quality (MGAB shows one of the best isotherm approximations). The following rank of the decrease of the adequacy (upon $\overline{D}$ criterion) of examined fitting equations in relation to the OC sorption isotherm approximation in the whole isotherm range was formed: MGAB > HZ > PD > GAB > AD > PN.

Keywords: Vapor-phase sorption isotherms; Organic sorbates; Soil and mineral sorbents; Approximation equations; Mathematical criteria of approximation adequacy

1. Introduction

The approximation of isotherms of vapor-phase sorption of organic compounds (OC) is a long-standing problem. It is especially difficult to solve in case of natural heterogeneous sorbents (soils, sediments, aquifers, etc.) since these sorbents contain sites with different sorption activity due to their content and structure complexity [1,2].

Generally, approximation of sorption isotherms is used for two reasons. The first cause concerns isotherm parameters which allow to characterize the properties of sorbate–sorbent systems. The second main reason is the possibility of the correct comparison of sorption values between different sorbate activities within a given system, as well as between different sorption systems of the same sorbate activity. To achieve the latter, it is crucial that the approximation equation is appropriate in the whole range of a given sorption isotherm. This is especially difficult for the heterogeneous sorbents in unsaturated conditions, when the sorption of OC can be realized by different mechanisms, occurring on mineral and organic surfaces, in sorbent pores, in the organic phase, etc.

The most commonly used equation for the approximation of isotherms of OC vapor sorption by geosorbents is still the

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